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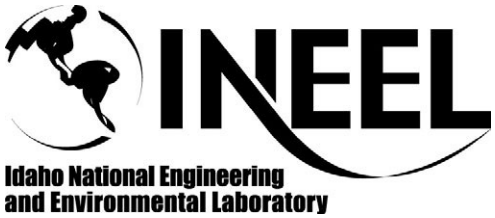

Soldification Of Acidic, High Nitrate Nuclear Wastes By Grouting Or Absorption On Silica Gel

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ABSTRACT

The use of grout and silica gel were explored for the solidification of four types of acidic, high nitrate radioactive wastes. Two methods of grouting were tested: direct grouting and pre-neutralization. Two methods of absorption on silica gel were also tested: direct absorption and rotary spray drying. The waste simulant acidity varied between 1 N and 12 N. The waste simulant was neutralized by pre-blending calcium hydroxide with Portland cement and blast furnace slag powders prior to mixing with the simulant for grout solidification. Liquid sodium hydroxide was used to partially neutralize the simulant to a pH above 2 and then it was absorbed for silica gel solidification. Formulations for each of these methods are presented along with waste form characteristics and properties. Compositional variation maps for grout formulations are presented which help determine the optimum "recipe" for a particular waste stream. These maps provide a method to determine the proportions of waste, calcium hydroxide, Portland cement, and blast furnace slag that provide a waste form that meets the disposal acceptance criteria. The maps guide researchers in selecting areas to study and provide an operational envelop that produces acceptable waste forms. The grouts both solidify and stabilize the wastes, while absorption on silica gel produces a solid waste that will not pass standard leaching procedures (TCLP) if required. Silica gel wastes can be made to pass most leach tests if heated to 600ºC.

INTRODUCTION

The sodium bearing waste (SBW) at the Idaho Technology and Engineering Center (INTEC) originated from the second and third cycles of spent nuclear fuel reprocessing, waste calcination, and decontamination activities [1,2]. It is an acidic liquid with high nitrate salts that is currently stored in the tanks at INTEC. Transformation of this waste into a disposable solid is among the important tasks of the Idaho Completion Project (ICP). Considerable research has been completed to provide the U.S. Department of Energy with information to select methods for disposal of SBW and any secondary process wastes. The four SBW liquid treatment alternatives under consideration are: 1. Cesium removal via ion exchange (CsIX), 2. Calcination, 3. Direct evaporation, and 4. Steam reforming. The liquid effluents from these treatment alternatives are expected to differ from one another and hence three solidification options of evaporation, grouting, and absorption are being evaluated. Anticipated compositions for the liquid waste streams arising from these processes are shown in Table 1. About 4 storage tanks for a total of just over 1 million gallons of SBW will be processed. Two of the tanks are designated at WM-180 and WM-189; thus, for this work the simulants were called SBW-180 and SBW-189. Plans have not been developed as to whether these 4 tanks will be processed separately or in a combination blend. These experiments tested the SBW-180 and SBW-189 separately as representing the extremes of acidity expected, SBW-180 being low (1 M) and SBW-189 being high (3M) acid.

The cesium removal via ion exchange (CsIX) process was proposed in 1998 [1] for stripping SBW of gamma radiation from cesium, so that the resulting liquid would be transuranic waste for solidification into grout or for absorption into silica gel [3,4]. The target repository for this waste form is the Waste Isolation Pilot Plant (WIPP).

The calcination and steam reforming operations are fluidized bed thermal processes to solidify the wastes and require off-gas scrubber systems. The New Waste Calcining Facility (NWCF) has operated for several years and the scrubber solutions have been well characterized. Pilot tests of the steam reformer system have been completed, but the scrubber effluent has not been characterized; however, it is expected to be similar to the NWCF scrub. Further, it is expected that the scrub solution will also be transuranic.

Direct evaporation is also a thermal process where the SBW is evaporated to the extent that is will solidify upon cooling. The overhead vapors would be sent for further evaporation and acid recovery in the Liquid Effluent Treatment and Disposal (LET&D) facility. This process would result in a highly acidic (12 M) liquid with relatively low activity. This waste could be sent to the Nevada Test Site, Hanford, or Envirocare of Utah for disposal.

Two solidification options involving fixation in a grout matrix and/or absorption on silica gel were evaluated through a series of experiments with simulated wastes (Table 1). As the table indicates, the waste simulants are essentially nitrate solutions of several cations. They differ significantly in their acid molarity, which is on the order of 1 molar for SBW-180, 2.86 molar for SBW-189, 1.97 molar for calcination scrubber solution (NWCF Scrub), and 12 molar for evaporator bottom acid (LET&D Acid). In view of these large variations in acid molarity, it became imperative to conduct a series of small-scale experiments to evaluate fixation of the waste streams as a function of acid neutralization. The waste loading is expected to differ in the two matrices of silica gel and grout, as a function of the extent of neutralization from weakly acidic to strongly alkaline. The mechanism of fixation in the silica gel and grout matrices are different. In the former matrix physico-chemical adsorption is predominated by dehydration caused by exchange of OH^- in silica gel for positive ions in the waste, whereas the waste - fixation in grout will largely occur by hydration reactions. The effects of cation valency and size on fixation mechanisms is expected to in turn influence the efficiency of waste retention in these matrices as a function of neutralization. In this regard effective retention of RCRA metals, cadmium, chromium, lead, nickel and mercury, and radioactive cesium is important, so that the waste forms comply with the waste acceptance criteria for disposal in WIPP [5,6]. Although, these elements are present in minor to trace abundance in the wastes of Table 1, the potential for hazard emerges from their rejection by the matrix due to higher valence and large ionic size, causing them to concentrate at the waste form surfaces as residual liquid (bleed water) or fibrous crystallites. Their concentration in the residual phases may be more imminent under higher waste loading, which is one of the factors for cost effective disposal. Thus, the overall intent of the small-scale experimental methods undertaken in this project has been to contribute towards optimization of the processing time, processing labor, equipment operation, waste loading and the quantity of the actual 55 gallon containers, while maintaining compliance of the waste form property with the waste acceptance criterion of no bleed water, for disposal in WIPP. The task specific methods in this report evolve from the results of previous tests, with the intent to mitigate empiricism in experimental work instructions. The scope of these new experiments is to place the empirical methodology on a firmer scientific platform. This approach has the potential to safe guard the large scale engineering process of waste immobilization from costly errors.

Table 1. Major Components of Waste Streams

Species	SBW-180 (M) [7]	SBW-189 (M) [8]	NWCF Scrub (M) [9]	LET&D Acid (M) [10]	Simulant Chemicals
Al	6.63E-1	7.11E-1	1.56E+0	5.60E-2	2.2M $Al(NO_3)_3$
B	1.23E-2	2.12E-2	5.42E-3		H_3BO_3
Ca	4.72E-2	7.30E-2	5.04E-2	1.00E-3	$Ca(NO_3)_2?4H_2O$
Cl	3.00-E2	2.06E-2	3.81E-2	5.00E-2	12.0 M HCl
Cu	6.97E-4	9.54E-4	1.56E-4		$Cu(NO_3)_2?2.5H_2O$
F	4.74E-2	1.38E-2	8.88E-2	7.00E-3	27.6 M HF
Fe	2.17E-2	2.68E-2	1.22E-2	3.00E-4	$Fe(NO_3)_3?9H_2O$
H	1.01E+0	2.86E+0	2.33E+0	1.20E+1	All acids
K	1.96E-1	2.25E-1	7.90E-2		KNO_3
Mg		2.21E-2	4.32E-3		$Mg(NO_3)_2?6H_2O$
Mn		1.95E-2	4.28E-3		$Mn(NO_3)_2$ [50% soln]
Na	2.06E+0	2.04E+0	6.03E-1	2.40E-2	$NaNO_3$
NO_3	5.01E+0	6.52E+0	8.24E+0	1.21E+1	15.8 M HNO_3
PO_4	1.37E-2	2.07E-3	3.10E-2		14.8 M H_3PO_4
Si		3.08E-4	3.68E-2		10g/L SiO in 5% HNO_3
SO_4	5.40E-2	1.07E-1	2.41E-2	1.00E-3	18.0 M H_2SO_4
Zn	1.05E-3	1.07E-3	2.47E-4		$Zn(NO_3)_2?6H_2O$
Zr	6.33E-5	3.57E-4	1.86E-2		$ZrO(NO_3)_2?3H_2O$

GROUTED WASTE FORMS

To meet the WIPP waste acceptance criteria, the waste form must be a solid with less than 1% free liquid and the radiation level must be less than 200 millirem (mR) for contact handled waste [5]. Recently, WIPP will accept RCRA waste code U134 for hydrofluoric acid provided the waste has no free liquids [6]. In addition, for local handling of the waste form, it is desired that grouted waste set up within no less than 1 week. The ASTM Vicat test was used to determine set time [11]. Free liquid was observed visually. Waste formulations meeting the early set and no free liquids were judged acceptable.

In the course of these experimental tests, two general formulations have emerged. The first formulation provided 40 weight% (wt%) loading of SBW to the total mass of the grout waste form. The test involved neutralization of the acidic waste by liquid sodium hydroxide and its subsequent cementation in the Portland cement plus blast furnace slag mixture. In the second formulation it was possible to increase the waste loading to 70 wt% by neutralizing the acidic waste with calcium hydroxide powder, which was followed by solidification in the Portland cement plus blast furnace slag matrix. The second formulation was recommended for disposal at WIPP for the CsIX SBW (Table 2).

For the NWCF scrub, the high waste loading formulation would not set up; however, the 40 wt% formulation was acceptable. It is thought that this is due to the very high nitrate content of this projected waste steam.

Due the extremely high acid in the LET&D condensate waste, solid calcium hydroxide is incrementally added while stirring to allow for cooling and to avoid overheating the solution. Using the solid calcium hydroxide avoids the extra liquid from 50% sodium hydroxide.

Table 2. Formulations Recommended For Further Evaluation.

Waste Steam	Mixing Method	Loading wt%	50% NaOH wt%	$Ca(OH)_2$ Wt%	Slag wt%	Portland Cement wt%	Silica Gel wt%	Viscosity cP	Density g/cm^3
SBW-180	1	72	0	5	0	23		38200	1.42
SBW-180	2	75	0	8.5	0	16.5		20500	1.43
SBW-180	3	72	3	7	6	12			1.47
SBW-180	4	65	6.6				28.4		1.10
SBW-189	1	68	0	5	0	27		27500	1.61
SBW-189	2	68	0	12.4	0	19.6		28900	1.51
SBW-189	3	66	9	7	6	12			1.53
SBW-189	4	57.1	12.9				30.0		1.28
Scrub	3	35	18	1	41.3	4.7		12000	1.70
Scrub	4	54.4	15.6				30.0		1.21
LET&D Acid	2	35		12.4	13.1	39.5			1.96

Mixing Methods: 1 – combine calcium hydroxide and cement and mix in one step
2 – neutralize with calcium hydroxide and then mix in cement and slag
3 – pre-neutralize with sodium hydroxide and mix remaining powders
4 – neutralize with sodium hydroxide and mix with silica gel

SILICA GEL WASTE FORMS

The use of silica gel to immobilize liquid waste is noted in the literature [12-15] In our case SBW was sprayed on silica gel in a rotary dryer system as shown in Figure 1. In this system the effective waste loading was as high as 89 wt% since most of the moisture was driven off. This waste form does not pass leach tests (TCLP) if required, but can be an excellent method to prepare the waste for transportation for further treatment elsewhere. If the waste and silica gel were heated to over 600°C [12], the waste form would pass TCLP for all toxic metals except chromium [3]. Since the waste and silica gel are very much like glass formers, minimal frit was added to make a T-glass at 1200°C. This glass waste form performed well in the Product Consistency Test (PCT) with a net silica gel/SBW loading of ~75 wt% in the glass [3].

For process simplicity and reduction of energy requirements, direct absorption without heating was explored in subsequent studies. For SBW-180, SBW-189, and NWCF scrub, direct absorption yielded up to 76 wt%, 74 wt%, and 75 wt% loading, respectively, without free liquid [4]. This silica gel waste form could meet the WIPP requirement of no free liquid with no leach requirements. However, silica gel waste forms would not be suitable for mixed low-level wastes that require TCLP. Again to reiterate, silica gel forms would be applicable as feed for vitrification processes.

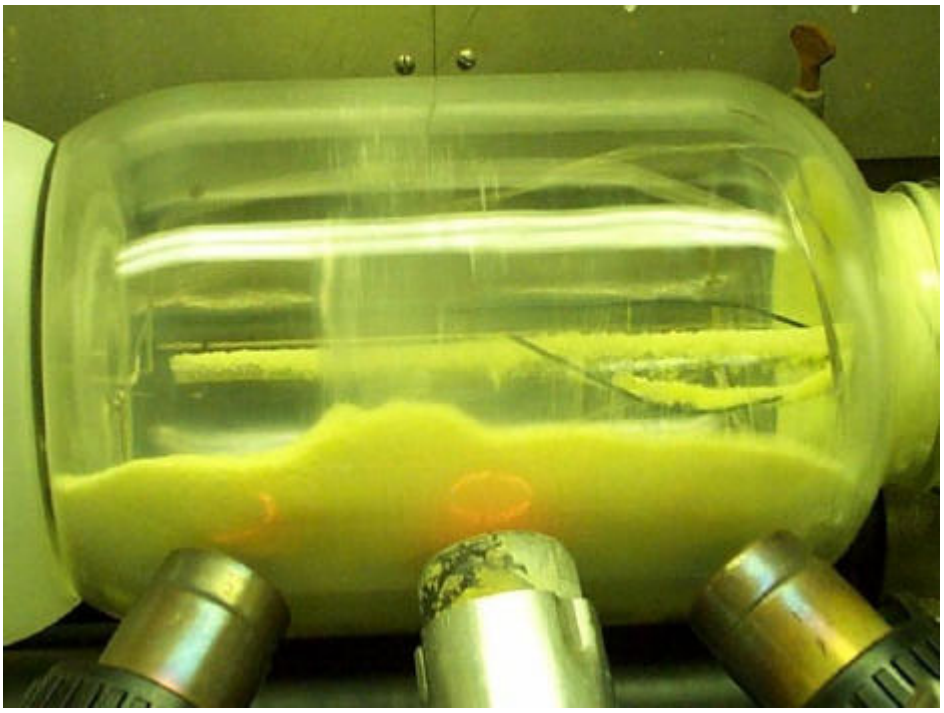

Figure 1. Laboratory rotary drier with hot air blowers for solidifying SBW on silica gel.

Figure 2. Typical grout (left) and silica gel (right) bottled samples. Note: Both are with SBW-189 simulant. The silica gel was directly loading with no pre-neutralization. The grout contains high slag with calcium hydroxide.

For the SBW-180 and SBW-189, the silica gel can be sprinkled on the surface of the liquid waste simulant. The silica gel readily absorbs the liquid and falls to the bottom of the sample bottle (Figure 2). For the NWCF scrubber solution, mixing is required due to the higher viscosity of the solution. Without mixing, the silica gel collects on the surface and may eventually fall to the bottom of the solution. In general, all three wastes can be directly absorbed on silica gel in the range of 65 wt% to 75 wt%. Samples at 65 wt% to 70 wt% usually exhibit excess silica gel remaining on top of the sample. For 70 wt% and above the waste approached saturation to the point where free liquid remained in the sample [4].

One finding of concern was the acidic vapor coming off the post-treatment silica gel [4]. When litmus paper was placed in the headspace of the sample bottle, it readily turned red in a matter of seconds, indicating acidic conditions. This presents a serious problem for this waste form in that the acid vapor in the headspace could condense and readily corrode the waste drum. To eliminate or reduce this problem, simulants were pre-neutralized to a pH over 2 and then mixed with the silica gel. For the samples made with pre-neutralized simulants (Table 2, Mixing Method 4), the acidic vapors were greatly reduced, i.e. the litmus paper did not turn red. Pre-neutralization reduced one problem, but presented a second one, i.e. the waste becomes more viscous when the acid is reduced. Thus, for wastes pre-neutralized to a pH over 2, mixing is required due the increase in viscosity and some precipitation. One other advantage for pre-neutralization is that the RCRA corrosive code can be removed from the waste form.

THE EFFECTS OF $CA(OH)_2$ AND NAOH NEUTRALIZERS ON GROUT FORMATION

Fixation of SBW-180, SBW-189 and NWCF Scrub, as a function of neutralizing agents, and cement/slag ratio was investigated. Of the three neutralizing agents, ammonium hydroxide, sodium hydroxide and calcium hydroxide, the last one has yielded more effective results. The results of $Ca(OH)_2$ addition to cement-slag and SBW-189 are shown in Figures 3 and 4. The $Ca(OH)_2$ was varied from 3.5 to 11 weight% as shown by horizontal boundaries on the diagram. The blocks indicated on Figures 3 and 4, delineate the compositional region for forming stable grouts with desirable processing properties of viscosity, grout setting time, waste loading and waste form shrinkage. Grout compositions outside of the marked region, were observed to be either very low in waste loading (below 50 wt%) or showed large shrinkage and registered 50 on the Vicat hardening scale. In the range of waste loadings above 52 wt% and under 71 wt%, the grouts also appear to remain soft with increase of slag/cement ratio beyond the 50% vertical boundary line on the diagram. Within the compositional block, the setting time was noted to increase with increase in waste loading towards higher $Ca(OH)_2$. Yet these grouts were noted to set to Vicat value of 1 within fifteen days. Rapid setting within three to five days seemed to occur for grout compositions occurring under the 7 weight% $Ca(OH)_2$ boundary line. About this boundary the waste loading of SBW-189 ranges from 60 to 68 weight%. The viscosity for these grouts ranges from 20000 to 35000 cp. The viscosity was noted to increase to about 40,000 cp in the directions of 4 wt% and 11 wt% $Ca(OH)_2$, from the 7 weight% $Ca(OH)_2$ median position. While the increase in viscosity towards 4 wt% $Ca(OH)_2$ boundary line is attributed to lower waste loading, a similar increase towards higher waste loading seems to be caused by increase in the $Ca(OH)_2$ to about 11 weight%. On the basis of these results an optimum compositional field for grout formation appears to fall within 7 and 5 wt% $Ca(OH)_2$ and also in the range of slag/cement ratio varying from 0 to 50 wt% slag. These results also apply to SBW-180 grout with differences caused by lower acid molarity in the latter waste stream. Because of low acid molarity of 1.0 when compared to nearly 3.0 (Table 1) for SBW-189, a higher loading of SBW-180 results under the same formulation ratio as for SBW-189. Thus, the region of stable grout formation for SBW-180 (Figure 4) also falls within the block outlined for SBW-189 (Figure 3). This difference in waste loading between SBW-180 and SBW-189 as a function of acid molarity is more evident in Figures 5 and 6. In these figures, the transformation of the liquid waste stream to grout through stages of gellation, liquefaction and slurry formation are noted with dependence of pH on total solids (cement+slag+$Ca(OH)_2$) addition to the waste stream. At low acid molarity as in SBW-180, variation in

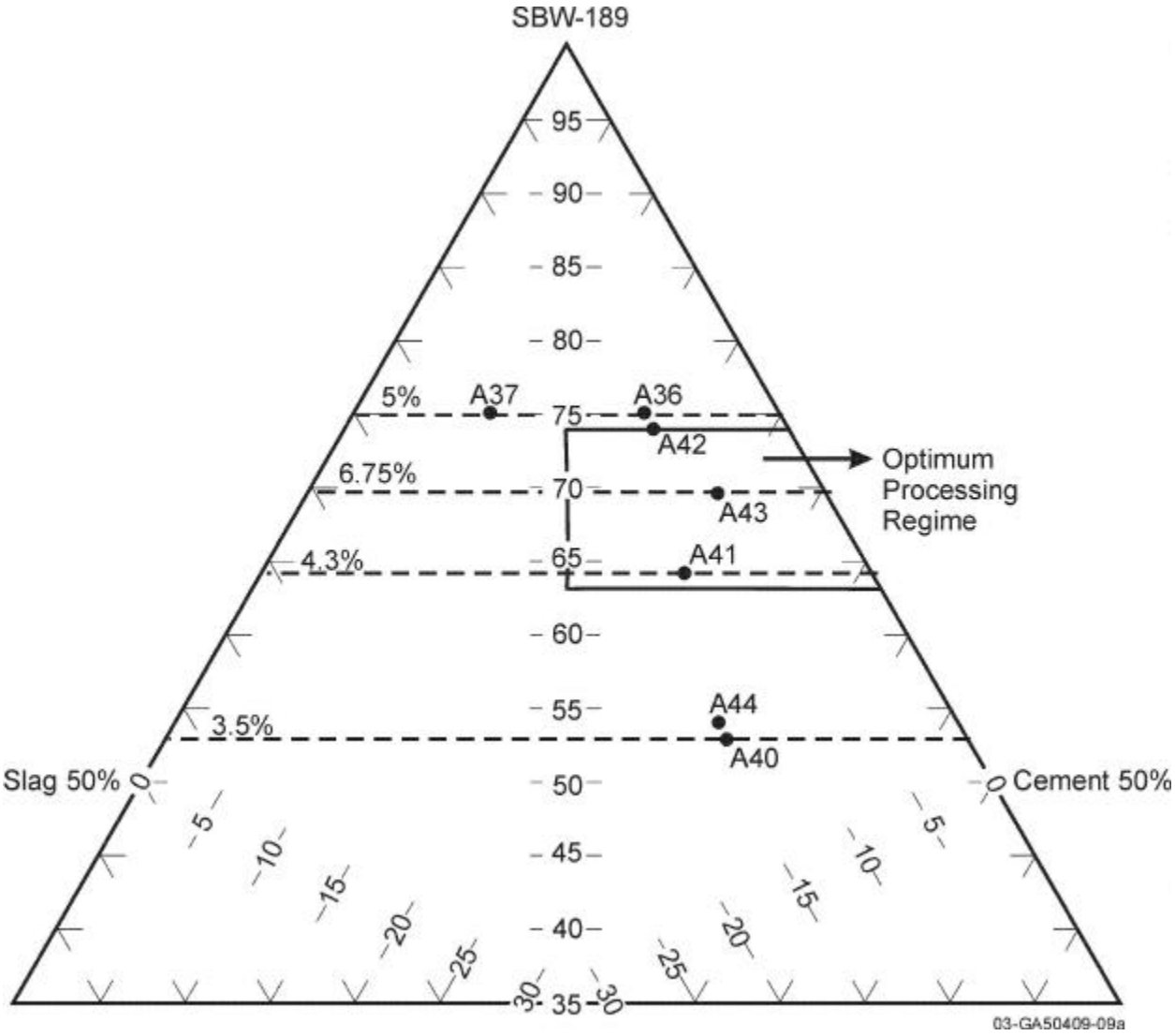

Figure 3. Grout formulation diagram with SBW-189 waste, slag, cement and $Ca(OH)_2$ as independent variables. $Ca(OH)_2$ weight% values are projected onto the ternary surface from the quaternary apex, at 5 wt%, 6.75wt%, 4.3 wt% and 3.5 wt% horizontal boundaries. The upper limit of slag/cement ratio is marked by the vertical boundary at nearly 50% slag:50% cement weight ratio. The upper and lower limits of waste loadings in the optimum processing regime are calculated as [%waste /(100% total solids - % $Ca(OH)_2$)] , thus the upper limit = 75% /(100 - 5) = 71.25 wt%, and lower limit = 65% /(100 - 4.0) = 62.4 wt%. SBW-180 are also processed within the same block.

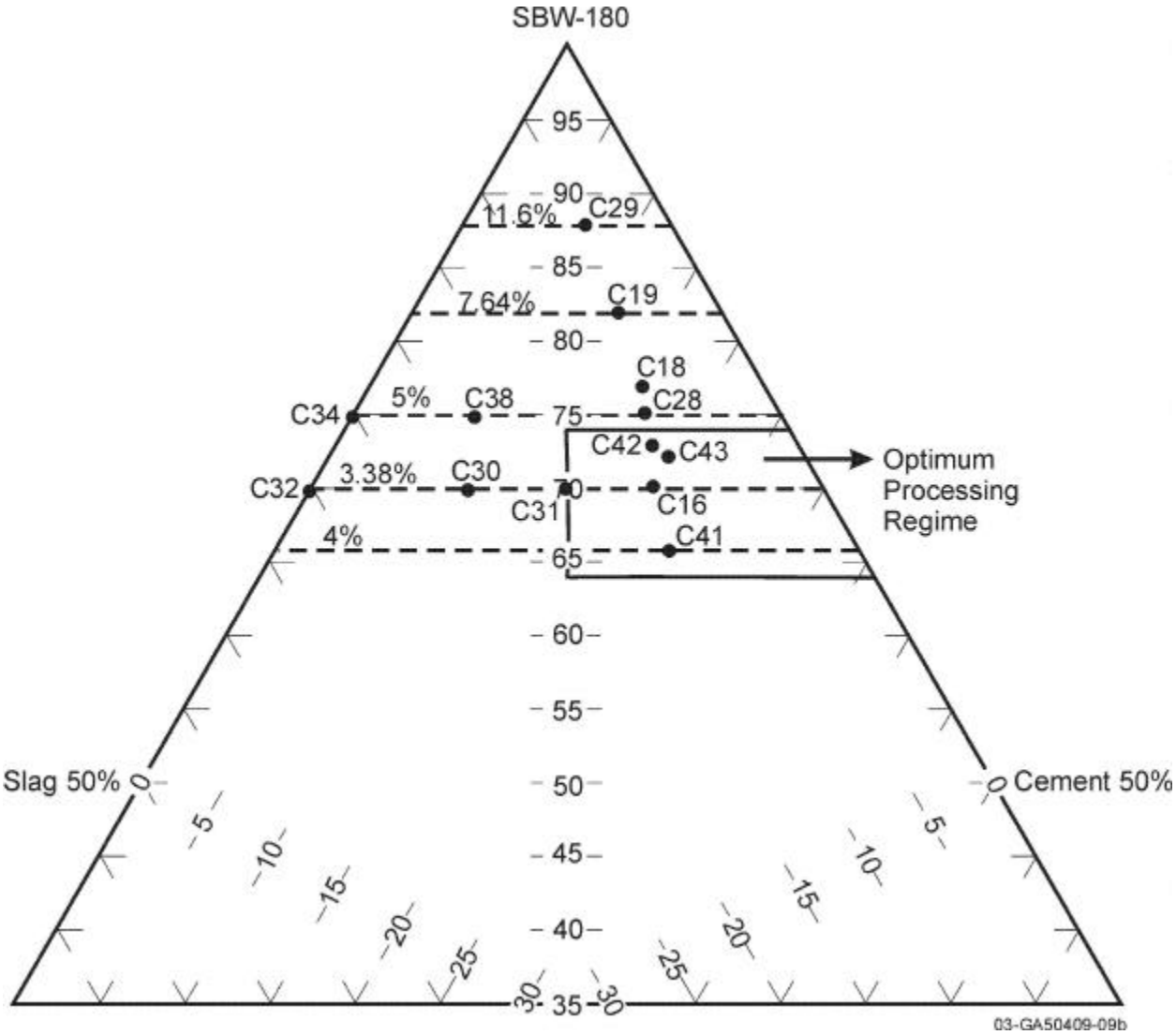

Figure 4. Grout formulation diagram with SBW-180 waste, slag, cement and $Ca(OH)_2$ as independent variables. $Ca(OH)_2$ weight% values are projected onto the ternary surface from the quaternary apex, at 11.6 wt%, 7.64 wt%, 5 wt%, 3.38 wt%, and 4.0 wt% horizontal boundaries. The upper limit of slag/cement ratio is marked by the vertical boundary at nearly 50% slag:50% cement weight ratio. The upper and lower limits of waste loadings in the optimum processing regime are calculated as [%waste /(100% total solids - % $Ca(OH)_2$)] , thus the upper limit = 75% /(100 - 5) = 71.25 wt%, and lower limit = 65% /(100 - 4.0) = 62.4 wt%. SBW-189 are also processed within the same block.

$Ca(OH)_2$ / ($Ca(OH)_2$ + Waste) from 10 wt% in C42 grout to 5.9 wt% in C41 grout, has a smaller influence on gellation, as a result the spread in the mass of total solids needed to achieve gellation is much narrower, from 43 to 50 grams for neutralizing 215 grams of SBW-180 to a pH of about 3 (Figures 5 and 6). Whereas for SBW-189 with acid molarity of 3.0 the spread in total solids mass ranges from 58 to 80 grams for the same variation in $Ca(OH)_2$ /waste ratio and similar neutralization pH of about 3. For both waste streams, liquefaction is reached at pH 7 with vigorous stirring and no further addition of total solids (Figures 5 and 6). The residence time for this reaction is on the order of ten minutes. This step is followed by subsequent addition of solids to form a stable grout with viscosity in the range of 10,000 to 20,000cp for both waste streams. The net result of these differences in the interaction with the total solids and $Ca(OH)_2$ is reflected in the lower waste loading for SBW-189 by about 3 to 5 wt% compared to that of SBW-180. From this exercise it may be concluded that a uniform formulation can be applied to waste streams showing variations in acid molarity with corresponding changes in waste loading. It remains to be observed how the RCRA metals will be immobilized by these formulations, the general results from preliminary studies have shown slag to be instrumental in the retention of RCRA components and hence slag was introduced to form the formulation block in Figure 3. These experiments were not extended to evaluate the behavior of NWCF Scrub solution. At present it is presumed that Scrub waste stream with molarity of 2.0 will show fixation behavior in grout that is intermediate between SBW-180 and SBW-189, and therefore, the formulation diagram in Figure 3 is predicted to apply to Scrub waste stream as well.

The results from the original matrix studies [4] show the high amounts of NaOH as a neutralizer did not yield good grouts for SBW-189 while keeping the waste loading high (70 wt% and above). In these experiments, liquid NaOH (50 weight to weight %) was used; thus, excess water is added to the waste. The grouts formed by NaOH neutralization considerably degrade or do not set up. The degrading characteristics are like large shrinkage, large cracking, and evolution of sodium nitrate fibers (Figure 7). Wastes that are fully neutralized to caustic and grouted at about 35 wt% are very stable, such as the NWCF scrubber grout. Also of note is that one process option being considered is to use solid NaOH to pre-neutralize the SBW prior to CsIX. This option is a recent development and has not been explored from a grouting standpoint.

Both $Ca(OH)_2$ and NaOH neutralized grouts were subjected to identical accelerated curing conditions (forced air drying). While the $Ca(OH)_2$ grouts have stably resisted the accelerated curing (Figures 8 & 9) for both SBW-180 and SBW-189, the rapid degradation of NaOH neutralized grouts became apparent in Figure 7. Accelerated curing was introduced by placing the grout cubes in an evacuating hood, where the suction of air from the hood possibly enhances the escape of vapor phase from the grout, resulting in the formation of sodium nitrate fibers that could be characterized by X-ray powder diffraction shown in Figure 10. At present it is speculated that such fibers should not be allowed to form, as they may potentially contain other alkalis like the radioactive cesium, or may even contain RCRA metals as occluded elements in the lattice that could be released with the dissolution of nitrate on contact with moisture. It has been possible to retard the formation of these crystalline fibers by curing the NaOH neutralized waste forms in an enclosed atmosphere, so that the vapor phase is contained within the waste form during its curing period. This impeded escape of vapor phase is accomplished by a simple method of enclosing the waste form in a sealed plastic bag. It remains to be tested how these waste forms will stabilize upon subsequent exposure to ambient conditions. Alternatively, it will be noted from Figures A and B (in the Executive Summary) that sodium nitrate layer formation is totally eliminated by introduction of slag and simultaneous decrease of waste loading by about 5 wt% in grouts A12 and A13 (Figure 8 and Table 6).

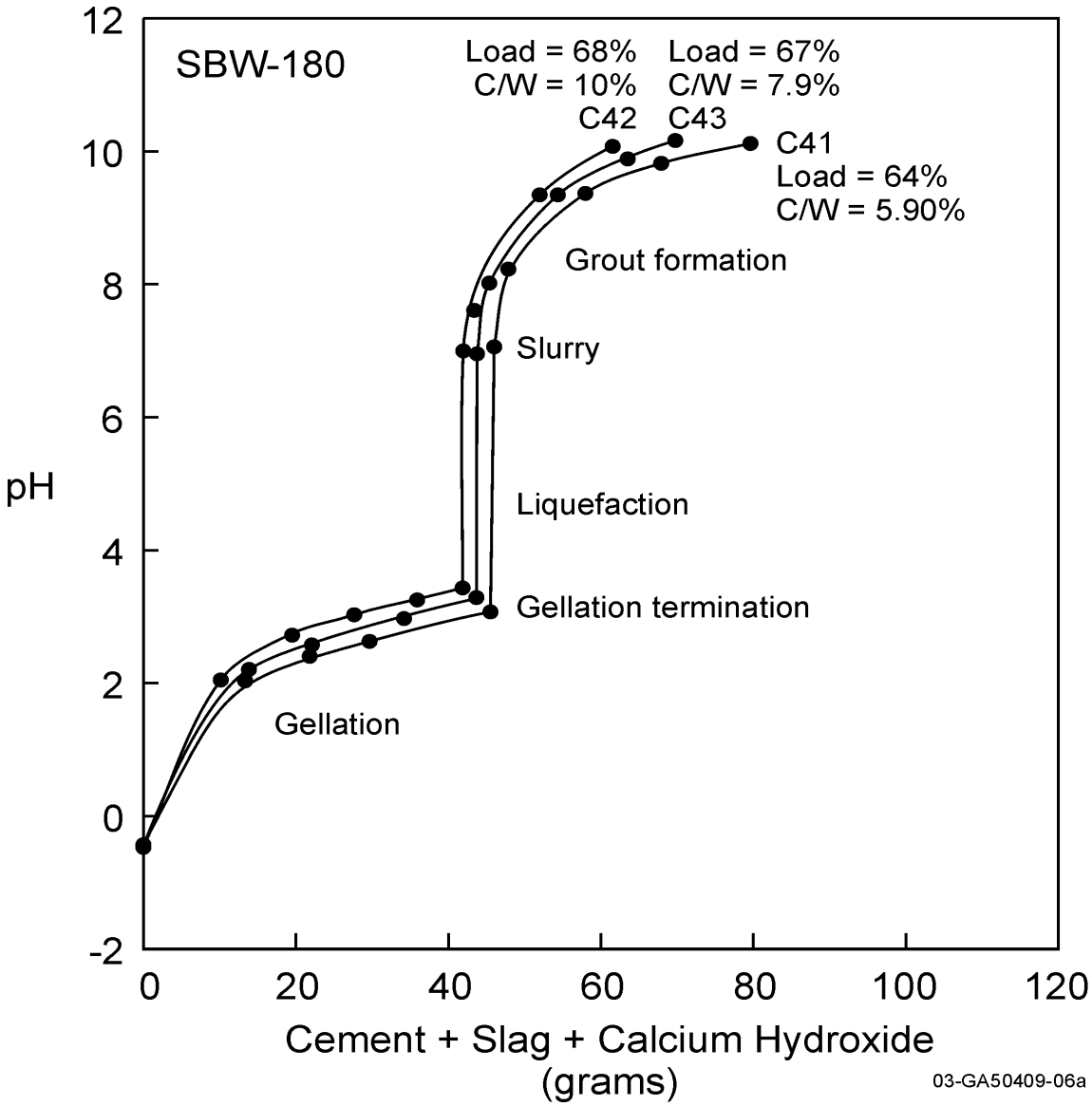

Figure 5. pH variations as a function of total solids addition to the SBW-180 waste solution. The first order phase change from gel to slurry is marked by a sharp vertical rise in pH and occurs with rigorous stirring of the gelatinous mass with no further addition of total solids. Subsequent additions of total solids lead to transformation of slurry to grout. Because of lower acid molarity of nearly 1 for SBW-180, these phase changes are less sensitive to variations in the neutralizer $Ca(OH)_2$, causing the trends to be closely spaced for SBW-180 fixation in the grout. C/W = $Ca(OH)_2$ / waste + $Ca(OH)_2$; Load = Waste Loading; C42, C43, C41 = SBW-180 grouts.

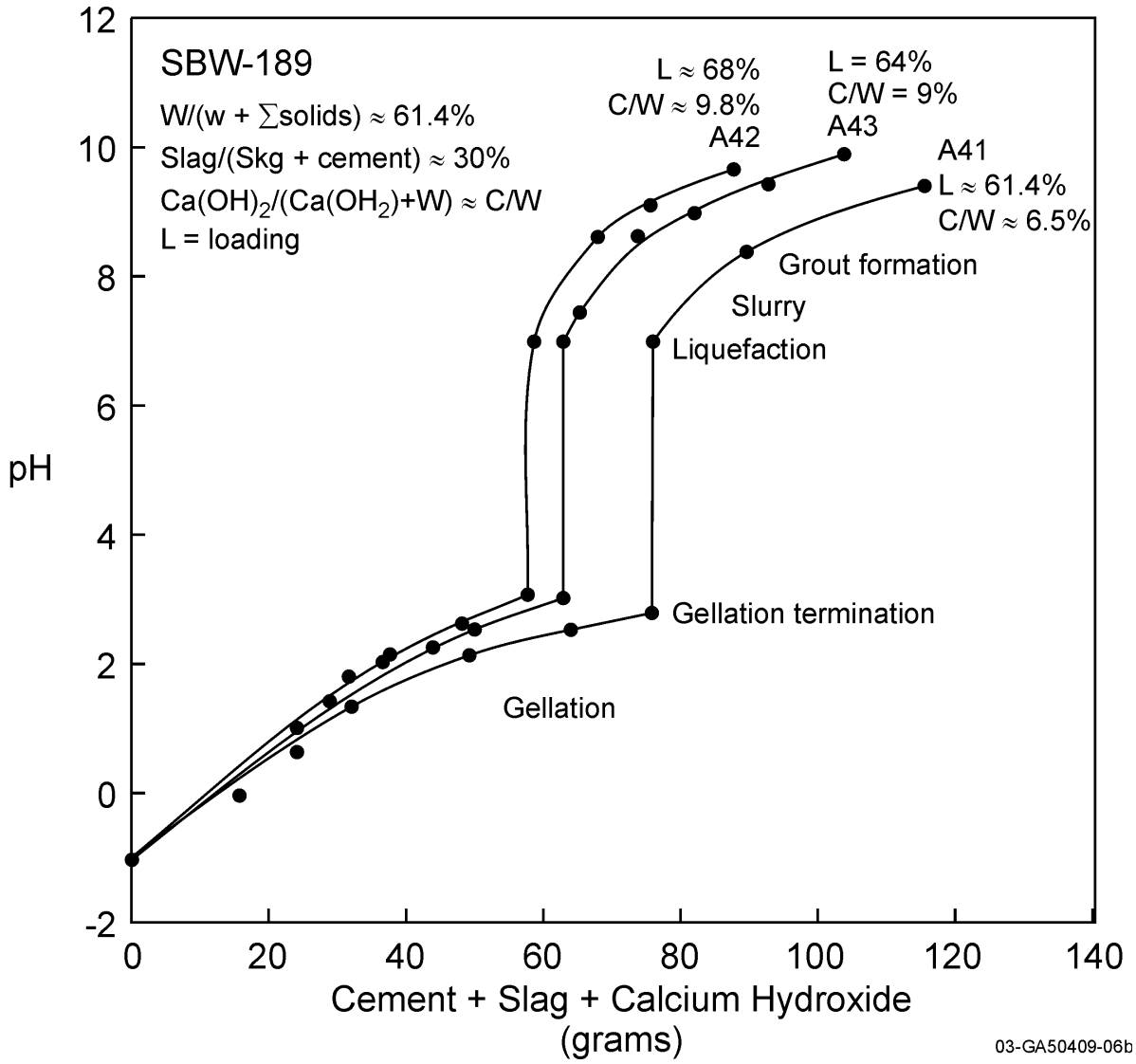

Figure 6. pH variations as a function of total solids addition to the SBW-189 waste solution. The trends are similar to the one shown in Figure 4. But due to higher acid molarity of nearly 2.86 for SBW-189, the phase changes are more sensitive to variations in the neutralizer $Ca(OH)_2$, causing the trends to be more widely spaced with respect to total solids addition for SBW-189 fixation in the grout. Both Figure 4 and Figure 5 trends correspond to 30 w% slag / 70 wt% cement ratio in Figure 3. A42, A43, A41, = SBW-189 grouts.

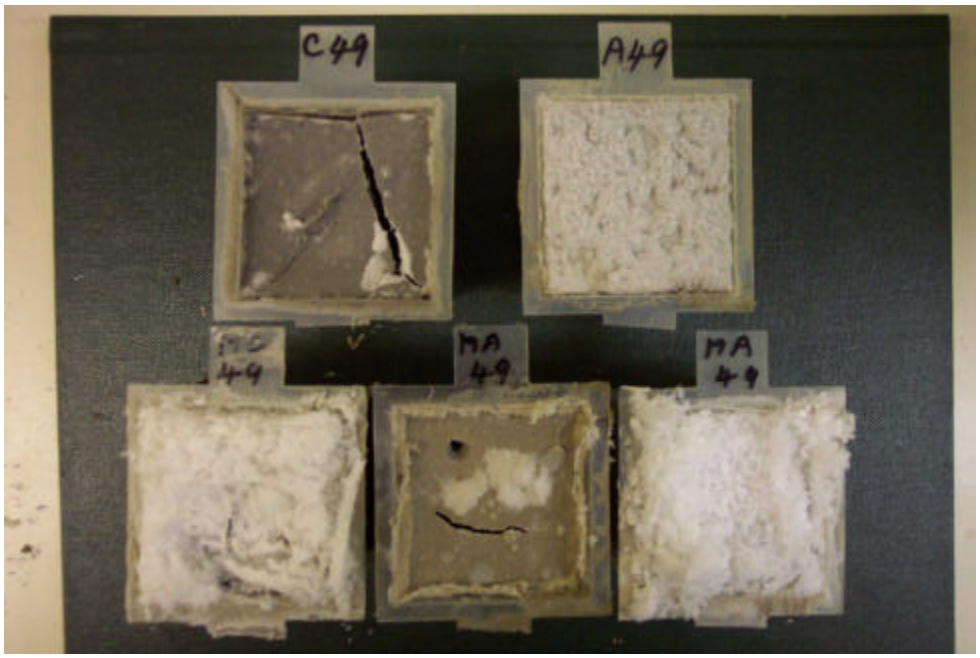

Figure 7. Grout cubes of SBW-189, (A49) and SBW-180 (C49) after neutralization by NaOH. Note the large dimensional changes due to shrinkage, cracking and white sodium nitrate crystallite formation on the surface.

Figure 8. Cured grouts of SBW-189. Left to Right : Top row: A12, A13, A40, Bottom row: A41, A42, A43, and A44. Surface whitening to varying degrees, caused by formation of about 1 mm thick sodium nitrate crystallite layer due to differences in the formulation. Compositions are shown on the formulation diagram Figure 3 and Table 6. Introduction of higher slag content (25 wt%) eliminated sodium nitrate vaporization and crystallization in grouts A12 and A13, and also imparted a brownish color to the grout matrix. Properties of these grouts are shown in Tables 7 and 8, and Figure 6.

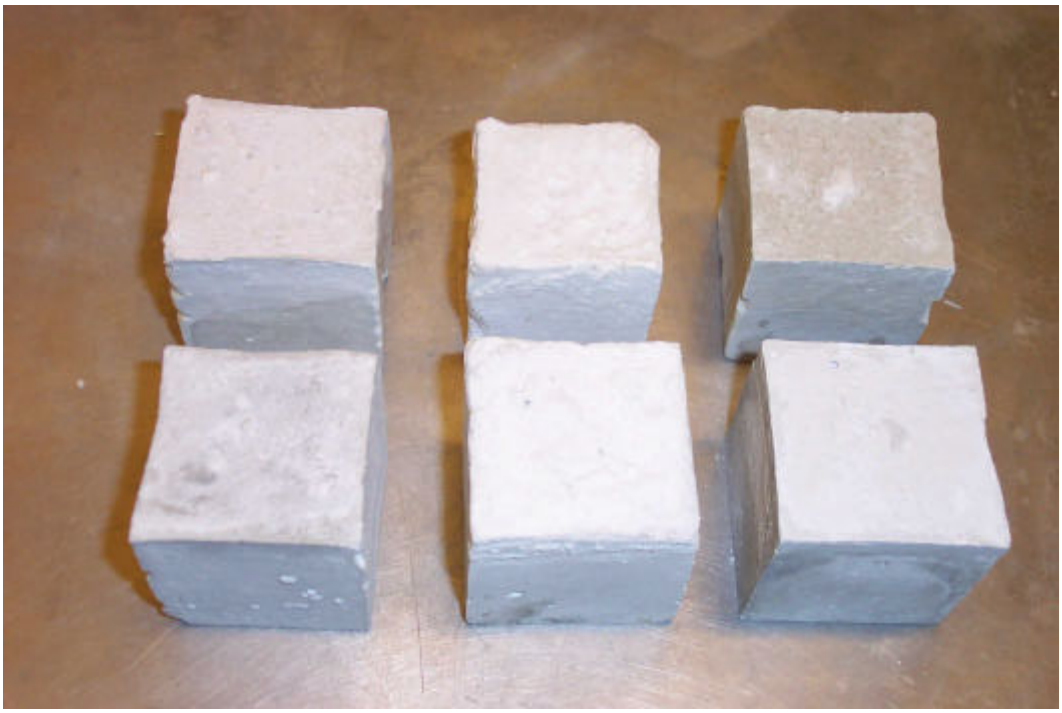

Figure 9. Cured grout of SBW-180. left to right: Top row: C16, C28 and C31, Bottom Row: C41, C43, C44. Properties of these grouts are shown in Tables 7 and 8, and Figure 5. Their relative compositions are shown on the formulation diagram, Figure 4 and Table 6.

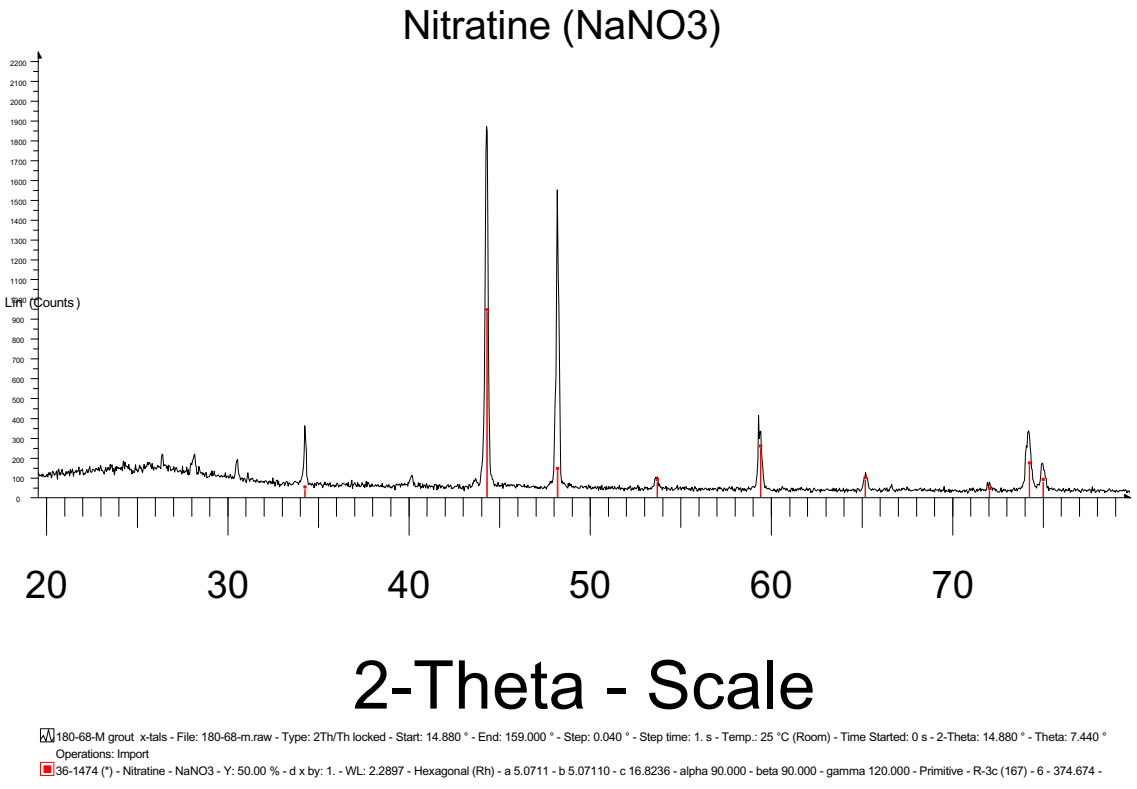

Figure 10. X-ray powder diffraction of fibrous crystallites forming on the surface of grouts in Figure 7.

MECHANICAL PROPERTIES OF GROUT

Exploratory tests were conducted to evaluate the quality of the waste form by yet another easily measurable property, the mechanical strength. The sensitivity of this property to chemical component additives has been documented in the commercial concrete industry [16], accordingly in the present study it is speculated that the changes in the formulation and waste loading would induce possible variations in the mechanical strength that may provide yet another parameter for assessing the stability of the grout. This contention is supported by the results gathered from preliminary tests shown in Table 4. In these tests, the cubes measuring 5cmX5cmX5cm were enclosed in a plastic bag and subjected to a dynamic uniaxial compression as shown in Figure 11. The force was increased at a steady rate of 267 lbs/sec, until

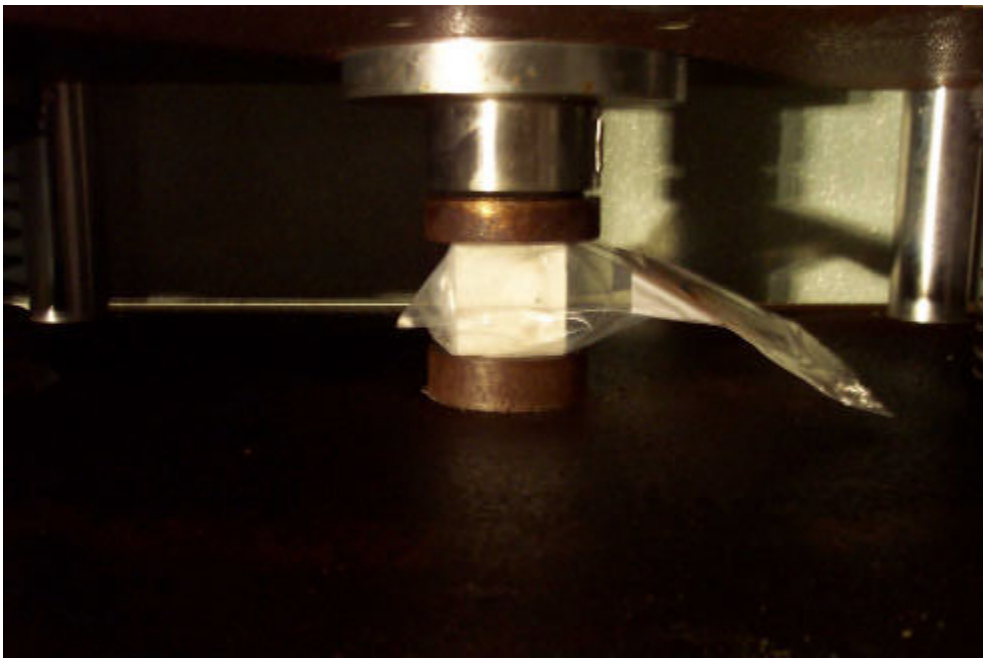

Figure 11. Position of the grout sample in the strength tester. The grout cube is placed in a plastic bag and then held between the discs for compression test in ambient atmosphere. The load is ramped at the rate of 150 lbs/sec until the breaking point of the sample.

failure of the sample. The force at the failure point and the time to failure were recorded. The mechanical strength was calculated as force / unit area and an approximate dependence of this property on formulation and waste loading is noted in Tables 3 and 4. As would be expected a general result emerges suggesting an increase in the mechanical strength with decrease in waste loading, for example, A40 and C41 grouts of SBW-189 and 180 record a higher mechanical strength of 2500 PSI (Table 4). At the low waste loadings of 51 wt% SBW-189 (A40) and 63 wt% SBW-180 (C41) in these grouts, the variations in the formulation (Tables 3 and 4) have little influence on the mechanical properties. However, the sensitivity to changes in formulation is apparent at higher waste loading of 68 wt%. For example the mechanical strengths of grout C28 and C16 are 1400 and 1500 PSI, and of A42 and A12 are 880 and 1190 PSI respectively. A noticeable change in the formulation of these grouts is in the $Ca(OH)_2$ neutralizer content, indicating decrease of mechanical strength with increase in $Ca(OH)_2$, although grout hardening is accelerated by increased addition of calcium hydroxide. From this difference in the calcium hydroxide effect it may be tentatively concluded that lowering of $Ca(OH)_2$ to 3.4 wt% (C16) from 10.20 wt% (C28) or to 3.2 wt% (A12) from 7.4 wt% (A42), prolongs the curing time, but also enhances the

mechanical strength. It may seem appropriate to consider decreasing the $Ca(OH)_2$ to a lower value of 3.5 wt% since, this component is already a part of Portland cement. It is present in the cement as CH in conjunction with C-S-H, where CH and C-S-H are abbreviations for calcium hydroxide and calcium silicate hydrate in the hydrated cement. During the curing period both these components interact to determine the modulus of elasticity of Portland cement [17]. Since, CH has a lower critical stress intensity factor (K_c) than Portland cement [17], excess addition of $Ca(OH)_2$ would very likely have a degrading effect on the mechanical behavior of the grout, as is observed in formulations C28 and A42 in Tables 3 and 4. Thus the testing of mechanical strength would not only contribute to evaluating the stability of the grout, which is a useful property for safe transportation of this nuclear material but it may also form the basis for introducing beneficial changes to formulations.

Table 3. Formulations, Viscosity, and Vicat Numbers for SBW-189 and SBW-180

Sample#	SBW-180 Wt%	SBW-189 Wt%	Ca(OH)2 Wt%	Cement Wt%	Slag Wt%	Vicat 7 day	Viscosity Centipoises X 10^3	Nitrate Layer Thickness
C16	67.98		3.4	20.03	8.58	0	20-25	0
C17	68.13		6.81	17.53	7.5	0	20-25	1 –2 mm
C18	71.66		7.16	14.81	6.35	0	20-25	10 mm
C19	76.43		7.64	11.14	4.77	50	8-12	
C27	67.62		3.38	20.29	8.69	0	12-20	1-2 mm
C28	68		10.20	15.23	6.52	0	25-30	0
C29	77		11.63	7.67	3.70	0	530-35	10 mm
C30	67.62		3.38	8.69	20.29	2	20-25	0
C31	67.62		3.38	14.49	14.49	2	15-20	0
C32	67.62		3.38	0	29	50	20-25	
C34	71.54		5.00	0	23.45	50	20-25	
C36	71.54		5.00	16.41	7.0	2	20-25	0
C38	71.54		5.00	7.03	16.41	10	20-25	0
C41	63.92		4.01	22.44	9.62	1	20-25	0
C42	68.4		7.59	16.76	7.20	0	25-30	0
C43	67.01		5.77	19.04	8.16	0	35-40	0
C44	60.17		1.8	26.60	11.43	1	30-35	0
A12		68	3.2	3.2	25.6	50	20-25	0
A13		68	3.2	6.4	22.4	30	25-30	0
A36		71.54	5.00	16.41	7.03	40	5-10	
A37		71.54	5.00	7.03	16.41	40	20-25	
A40		51	3.56	31.84	13.64	2	30-35	0
A41		61.36	4.29	24.03	10.30	1	30-35	0
A42		68	7.4	17.0	7.60	7	30-35	0
A43		64.2	6.75	22.30	6.68	1	35-40	0
A44		53.52	1.34	31.63	13.53	1	15-20	0

Table 4. Mechanical Properties of Grout Cubes

Grout #	Waste loading wt%	Density g/cm^3	Area inches^2	Force lbf	Strength psi	Breaking Time sec
C16	67.98	1.43	4.0	6000	1500	49.6
C28	68	1.51	2.25	3130	1390	62.2
C31	67.2	1.38	4.0	4080	1020	30.3
C41	63.92	1.58	3.0	7680	2500	85.1
C43	67.01	1.32	4.0	5010	1250	35.1
C44	60	1.44	4.0	6430	1600	36.4
A40	51	1.76	4.0	10060	2510	47.4
A41	61.36	1.64	4.0	4940	1230	30.6
A42	68	1.44	4.0	3550	880	34.8
A43	64	1.54	4.0	4640	1160	30.0
A12	68	1.61	4.0	4780	1190	69.5
A13	68	1.66	4.0	4460	1110	32.0

GROUTING OF PRE-NEUTRALIZED SODIUM-BEARING WASTE

Towards the end of the fiscal year, it was noted that the separations research was finding that the sodium-bearing waste needed to be pre-neutralized in order to reduce or prevent degradation to the cesium ion-exchange sorbent. The latest intent is to use sodium hydroxide to partially neutralize the waste streams to 0.5 Molar. For the SBW-189 stream simulant, it takes 114 mL sodium hydroxide to bring 1 L to 0.5 Molar. With both the SBW-180 and SBW-189 wastes now at 0.5 Molar, the question becomes, "Can a common grout formulation be found for both wastes?" A limited number of grout samples were prepared at the end of the year to determine if this is possible. The short answer is, "Yes." Table 5 shows the preliminary common formulation used for SBW. In the case of SBW-189 grout, 66 wt% is SBW and 9 wt% sodium hydroxide to partially neutralize; thus, 75 wt% would be the incoming liquid to be solidified. In the case of SBW-180 grout, 72 wt% is SBW and 3 wt% is sodium hydroxide, again for 75 wt% to be grouted. The remaining powders are 7 wt% calcium hydroxide, 6 wt% slag, and 12 wt% Portland cement. These formulations were successfully used in the 55-gallon drum pilot plant mixer tests [18]. The formulations proved to be self-leveling in the drums and readily thickened to a clay-like compound. It is thought that the blast furnace slag promotes the self-leveling property. Without slag, the grout is much thicker. A detailed formulation study is needed to confirm these preliminary findings and determine the operational envelop.

Table 5. Pre-Neutralized SBW Grout Formulation from CsIX Process

Component	SBW-180 (wt%)	SBW-189 (wt%)
Sodium-Bearing Waste	72	66
Sodium Hydroxide (50%)	3	9
Calcium Hydroxide	7	7
Blast Furnace Slag	6	6
Portland Cement	12	12

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

A large part of this report has concentrated on the methodology for developing waste forms for acidic, high nitrate waste effluents. At the hindsight, the problem may appear to be very simple because the only qualifying criterion for disposal in the Waste Isolation Pilot Plant is that the waste forms be devoid of any free liquid. For grouted forms, a simple empirical approach of mixing Portland cement and waste streams may then appear to meet the demands for forming a suitable grout. The project was commenced with this intent, where both ad-hoc tests and tests based on statistical design led to results ranging from hardened grouts to unsetting grouts and to grouts with discolored bleed liquids. Owing to uncertainties in the results, the method was progressed towards examining the roles of the various components like the waste stream composition, the slag/cement ratio, and the total proportions of acid neutralizing agents. In view of the nearly four independent components involved in the determination of the grout stability and waste loading, the statistically designed component proportions were plotted on a triangular composition net, which then was used to determine the future course of compositional directions for introducing desirable changes in the grout properties. This method has led to minimizing production of secondary wastes by enabling preparation of grouts with predictable properties. The compositional boundaries for formation of stable grouts are thus determined to span from 100% cement to 50% cement / 50% slag for waste loadings ranging from 55 wt% to 70 wt% (Figures 3 and 4). Within these boundaries, the stability of the grout is influenced by yet another factor: the acid molarity of the waste effluents.

Noting that the grout properties in the construction industry are related to water / cement ratio, [16, 19, 20] where the liquid, in this case water has a neutral pH, it is natural to consider neutralizing the acidic waste effluents. The three commonly available neutralizing agents NH_4OH, NaOH or $Ca(OH)_2$ were tested for this purpose (Table 5). As the compositions would indicate, ammonium hydroxide is perhaps the most suitable agent, for there are no common cationic effects involved between the neutralizer, and the waste or cement+slag. However, its odor and high vapor pressure, placed stringent restrictions on its use in a normal laboratory setting. As a result the use of this reagent was considered only to explore the mechanism of acidic waste fixation in a grout. Through this important basic experimental exercise, the steps of gellation, liquefaction, and neutral (pH=7) slurry formation became apparent for eliminating the bleed liquid. Of the remaining two neutralizing agents, experiments showed $Ca(OH)_2$ to be more effective than NaOH in the elimination of bleed liquid and in the hardening of grout. Two problems were noted with the use of NaOH, 1. gels formed by direct addition of NaOH to the waste rapidly peptized to become liquid again, which could be an important cause for the occurrence of bleed liquid, and 2. sodium nitrate fibers appeared to grow on the surface during the curing period, due to additional introduction of sodium ions to the already sodium nitrate enriched waste effluents, these nitrate fibers in several grouts seemed to diminish curing, leading to large dimensional changes, cracking and softness. The third approach of $Ca(OH)_2$ addition to the liquid waste effluent seemed to eliminate the second part of the problem but bleed liquid continued to persist in several grouts, once again indicating incomplete hydration reactions due to the interaction of the cement with $Ca(OH)_2$ enriched gel. This problem was eliminated by changing the addition of $Ca(OH)_2$ from directly to the waste effluent to blending it with the cement or cement + slag in powdered form. Subsequent addition of the blended powder to the waste effluent revealed all the mechanistic steps for grout formation (Figures 5 and 6), total elimination of bleed liquid and rapid setting of the grout with minimal dimensional change during curing. Since, the Portland cement itself contains calcium hydroxide, a limited addition of calcium hydroxide was considered necessary to avoid potential prolongation in the hardening of the grout. Preliminary experiments have pointed to an upper limit of about 10 wt% $Ca(OH)_2$. The compressive strength tests (Table 4) have also pointed to weakening of the grout with increases in $Ca(OH)_2$. Thus the optimum $Ca(OH)_2$ addition is on the order of 3.5 wt% for formation of desirable grouts.

In order to reduce waste/grout mixing operational complexity, it is desirable to develop a uniform grout formulation. By using the formulation diagrams (Figures 1 - 4) and improving on them in the future, it

should be possible to find a common formulation for all SBW effluents, especially after pre-neutralization. Two uniform formulations may be considered: 1) An common general formulation or 2) a common cement powder formulation. For example, the general formulation would be where following neutralization, all SBW wastes would be grouted at a certain waste loading using the same calcium hydroxide to slag to cement ratio. In the second case, the waste loading may change for each waste, but the calcium hydroxide to slag to cement ratio would remain constant. The first method would be preferable, but even the second would reduce complexity. A cost advantage may be found in adopting a uniform formulation technology based on the development of formulation maps (Figures 1 - 4). The results obtained from these formulation maps have successfully been applied for the pilot plant scale up process.

Table 2 summarizes the formulations recommended for treatment of acidic, high nitrate wastes. The formulations provide a range of processing options such as pre-neutralization and pre-blending all powders prior to mixing with the liquids. Such processes will need to be "tailored" for the process, mixer, and equipment selected.

REFERENCES

1. Losinski, S. J., C. M. Barnes, and B. K. Grover, "CsIX/TRU Grout Feasibility Study," INEEL/EXT-99-00034, July 1999.
2. Boardman, R. D., "Other Separation Processes – Alternative Separation Technologies for Treating Sodium – Containing Acidic Wastes", in Separation Techniques in Nuclear Waste Management, edited by T. E. Carleson, N. A. Chipman and C. M. Wai, CRC Press, N.Y., 109-120, 1995.
3. Herbst, A. K., et al., "Idaho Nuclear Technology and Engineering Center Low-Activity Waste Process Technology Program FY-2000 Status Report, " INEEL/EXT-2000-01167, October 2000.
4. Herbst, A. K., et al., "Idaho Nuclear Technology and Engineering Center Sodium Bearing Waste Treatment Research and Development FY-2002 Status Report, " INEEL/EXT-02-00985, September 2002.
5. U.S. Department of Energy, "Waste Acceptance Criteria for the Waste Isolation Pilot Plant," Rev. 7, DOE/WIPP-069, November 8, 1999.
6. Bosley, J. B., electronic communication (e-mail), "No Free Liquid/U-134," forwarding electronic communication from S. Johansen of WIPP, January 29, 2003.
7. Christian, J. D., "Composition and Simulation of Tank WM-180 Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center," INEEL/EXT-2001-00600, May 2001.
8. Batcheller, T. A., and D. D. Taylor, "Characterization of Tank WM-189 Sodium Bearing Waste at the Idaho Nuclear Technology and Engineering Center," INEEL/EXT-02-01171, September 2002.
9. Barnes, C. M., et al., "Calcination with MACT Upgrade Process Design," Engineering Design File 3387, February 2003.
10. J. A. Nenni, "Balance of Plant Sample Data Compilation," Engineering Design File 2506, February 2002. LET&D Acid Composition based on LET&D Bottoms Tank – WLL-195 Sample Log #9905042.
11. American Society for Testing and Materials, "Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle," ASTM C191-01a.
12. Nardova, A. K. and Tumanova, O. S. , "Examination of Mechanism of Saturation of Silica Gel with Metals at High Temperatures", Spectrum 1996 Proceedings.
13. Cicero-Herman, C.A. et al, "Silica Gel Treatment For Stabilization of Radioactive Materials", Westinghouse Savannah River Company Report WSRC-TR-97-0095, March 1997.

14. Maatman R. W. et al, "The Exchange of Twenty Metal Ions with the Weakly Acidic Silanol Group of Silica Gel," J. of Phys. Chem. **68** No 4 pp757 April 1964.
15. Meites L. et al, "Exchange of Na+ for the Silanolic Protons of Silica."J. inorg. nucl. **33**, Oct 1971 pp.1293-1299.
16. Hewlett, P. C., Lea's Chemistry of Cement and Concrete, John Wiley & Sons, 4th Edition, 1998, 1053 pp.
17. Beaudoin, J. J., in Materials Science of Concrete, edited by J. Skalny, J. Gebauer, and I. Odler, Amer. Ceram. Soc. publication 2000, p. 131.
18. Scholes, B. A., et al., "Out-Of-Drum Grout Mixer Testing with Simulated Liquid Effluents Originating from Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center," INEEL-EXT-03-01095, September 2003.
19. Pann, K. S., T. Yen, C. W. Tang, and T. D. Lin, New strength model based on water-cement ratio and capillary porosity. Materials Journal, Vol. 100, 2003, p. 311.
20. Kosmatka, S. H., and W. C. Panarese, Design and Control of Concrete Mixtures, Portland Cement Association (PCA), publication, 1994, p. 77.

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